Simultaneous Determination of Lead and Zinc in Iron and Steel by Cathode Ray Polarographic Method

Simultaneous Determination of Lead and Zinc in Iron and Steel by Cathode Ray Polarographic Method*

Michiko NAMIKI and Hidehiro GOTÔ

The Research Institute for Iron, Steel and Other Metals

(Received January 13, 1971)

Synopsis

In order to determine microamounts of lead and zinc in iron and steel, a highly sensitive and rapid cathode ray polarography was studied and the examinations were made of supporting electrolyte, treatment after removal of iron, effect of coexisting elements, and peak potentials. The method was then applied to iron and steel samples. In this method, the sample is decomposed with hydrochloric and nitric acids, which is evaporated to dryness, the residue is dissolved in 5N hydrochloric acid, and iron is extracted with methyl isobutyl ketone. A part of zinc that transited to the organic layer is back-extracted with 6N hydrochloric acid and this acid solution is mixed with the aqueous layer. This layer is evaporated to dryness, methyl isobutyl ketone is decomposed with nitric and perchloric acids, and the layer is again evaporated to dryness. This procedure is repeated three times. The cooled residue is submitted to polarography with 0.5M phosphoric acid as the supporting electrolyte, gelatin is added, and the wave height at peak potential is measured at −0.52 V *vs* S.C.E. for lead and at −1.17V *vs*. S.C.E. for zinc.

This method enabled the determination of lead and zinc in synthetic and actual samples to the order of 0.00x%, the standard deviation being ±0.00017% for lead and ±0.00063% for zinc, and the coefficient of variation being 11.3% for lead and 15.1% for zinc.

I. Introduction

Photometric determination with dithizone[1]~[3] is often used for the determination of microamounts of lead and zinc in iron and steel. This method is very sensitive but is affected by the presence of other elements, the purification of sample requires a somewhat long time, and the procedure is rather complicated.

Separatory extraction of lead and zinc from main components like iron and steel[4], and polarographic measurement using dithizone, with ammonium acetate or ammonium thiocyanate as the supporting electrolyte, have also been practiced but this procedure is also complicated. There are also various polarographic

---

* The **1474th** report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the Japan Analyst, **17** (1968), 43.

(1) E.B. Sandell, *Colorimetric Determination of Trace of Metals* (1950), p. 420.
(2) E.B. Sandell, ibid., p. 630.
(3) H. Gotô, Y. Kakita and S. Suzuki, *Colorimetric Determination of Metals* (1956).
(4) Japan Ind. Standard, M8229 (1964).

determinations of lead[5],[6] and zinc[7] in which different supporting electrolytes are used.

Simultaneous determination of lead and zinc in iron ore and in iron and steel by DC polarography has been reported by the present authors[8]. In order to make further the microamount determination, simultaneous determination of lead and zinc by cathode ray polarography was examined and it was found that a satisfactory result could be obtained by removal of iron, the main component, by extraction with methyl isobutyl ketone[9] and by using phosphoric acid[10],[11] as the supporting electrolyte.

II. Reagents and apparatus

1. Reagents

Standard lead solution: A solution of 0.7995 g of special grade lead nitrate dissolved in water is diluted exactly to 500 ml. One ml of this solution contains 1 mg of lead and this solution is diluted with water to make a solution of 10 μg/ml.

Standard zinc solution: A solution of 0.5 g of special grade metallic zinc dissolved in ca. 10 ml of hydrochloric acid is diluted with water exactly to 500 ml. One ml of this solution contains 1 mg of zinc and this solution is diluted with water to make a solution of 10 μg/ml.

5M phosphoric acid: Special grade phosphoric acid is diluted with water.

Gelatin solution: 0.2% solution, to which is added 2 g (per 500 ml) of thymol to prevent putrefaction.

Methyl isobutyl ketone, hydrochloric acid, nitric acid, perchloric acid, hydrogen peroxide, and potassium permanganate used were of all commercial products of special grade.

2. Apparatus

Yanagimoto's Polarovision Model PE-20 was used, with mercury pool as the anode. Characteristics of dropping mercury electrode were as follows: m= 6.69 mg/drop for lead sweep and m=5.92 /drop for zinc sweep, and natural drop rate was 5.3 sec. Measurement was carried out at room temperature.

(5) R.C. Rooney, Analyst, **90** (1965), 545.
(6) V.P. Gladyshev, G.P. Chinaeva and A.M. Ustimov, J. Anal. Chem. USSR, **20** (1965), 300.
(7) K. Itsuki and M. Nagao, Japan Analyst, **9** (1960), 836.
(8) H. Gotô and M. Namiki, J. Japan Inst. Metals, **31** (1967), 5.
(9) H. Gotô, Y. Kakita and T. Furukawa, Nippon Kagaku Zasshi, **79** (1958), 1513.
(10) H. Shirai, Japan Analyst, **9** (1960), 206.
(11) K. Nishimura and T. Imai, ibid., **13** (1964), 423.

III. Experimental and results

1. Examination of supporting electrolytes

(i) 1N sodium hydroxide

Since 1N sodium hydroxide was used in the previous DC polarography[8], this was used in the present cathode ray polarography but it was found that the reduction wave of a minute amount of iron (II) dissolved in sodium hydroxide was close to the peak potential of zinc, making it impossible to determine zinc, and the simultaneous determination was difficult.

(ii) Electrolytic conditions using phosphoric acid

Phosphoric acid was then examined as a supporting electrolyte for the simultaneous determination of lead and zinc. Concentration of phosphoric acid was made 0.4 M, 30 μg each of lead and zinc were added, and the total volume was made 50 ml, which was submitted to polarography. In this case, clean peaks were observed when the measurement was carried out under the following conditions, and so, the subsequent experiments were carried out under these conditions.

Electrolytic condition

	Pb	Zn
sweep rate	0.3 V/sec	0.3 V/sec
initial voltage	–0.4 V	–1.0 V
sweep start	2.0 sec	2.0 sec
sweep stop	3.5 sec	3.5 sec
peak potential	–0.67 V *vs.* Hg	–1.34 V *vs.* Hg

The wave form obtained under these conditions is shown in Fig. 1 for lead and in Fig. 2 for zinc.

2. Effect of phosphoric acid concentration

Forty micrograms each of lead and zinc were placed in 50-ml measuring flask and phosphoric acid was added in varied concentrations of 0.1～2M to examine

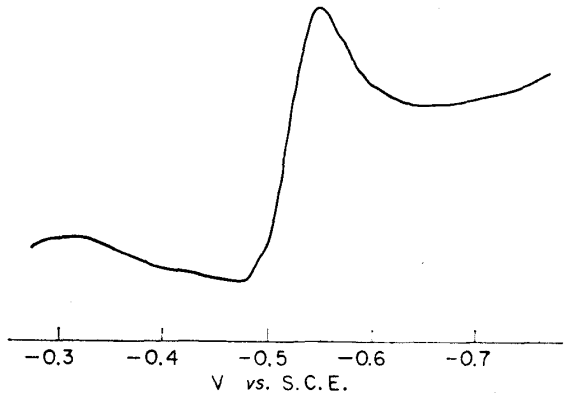

Fig. 1. Polarogram of Pb.
Initial voltage: –0.3V, Sweep rate: 0.3 V/sec, Sweep start: 2.0 sec, Sweep stop: 3.5 sec, Supporting electrolyte: 0.5 *M* H_3PO_4.

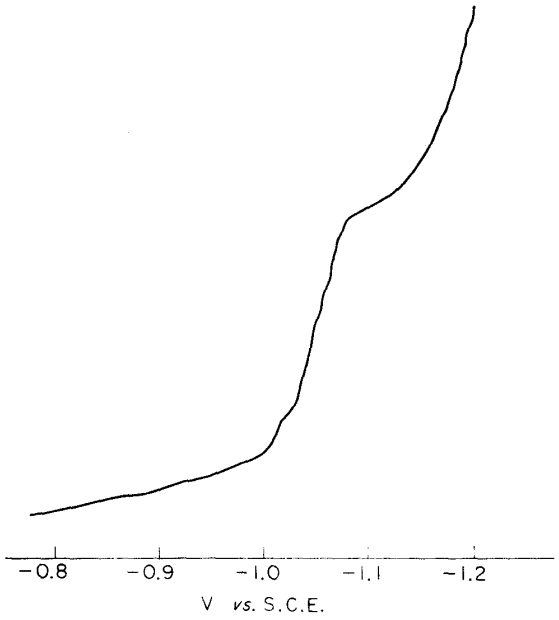

Fig. 2. Polarogram of Zn.
Initial voltage: −0.3V, Sweep rate: 0.3 V/sec, Sweep start: 2.0 sec, Sweep stop: 3.5 sec, Supporting electrolyte: 0.5 *M* H_3PO_4

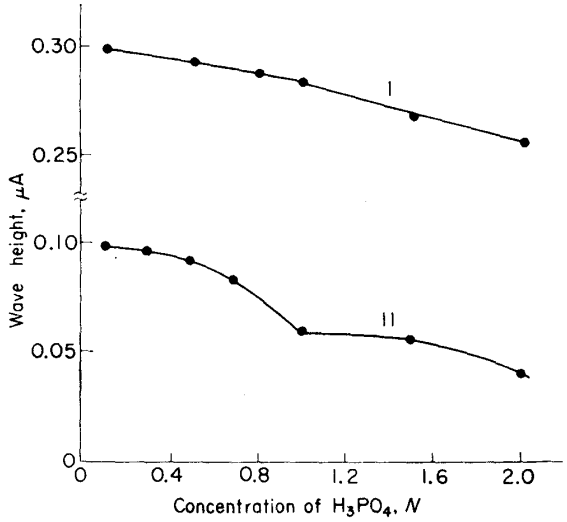

Fig. 3. Effect of the concentration of phosphoric acid.
I: Zn (40 μg), II: Pb (40 μg).

the effect of acid concentration.

As shown in Fig. 3, there is no great change in the range of 0.1∼0.5M but the wave height tended to decrease above this concentration. Therefore, 0.5M phosphoric acid was used in the subsequent experiments, in careful consideration of the application of this method to iron and steel.

3. Relationship between wave height and quantity of lead and zinc

In order to examine this relationship, 0∼80 μg each of lead and zinc were

placed in 50-ml measuring flasks, 5 ml of 5M phosphoric acid and 1 ml of 0.2% gelatin solution were added to each, and the whole volume was brought to 50 ml with water. A part of this mixture was placed in an electrolytic cell and nitrogen was passed through the solution to remove oxygen. The resultant solution was submitted to polarography under the above-mentioned conditions and the wave height of lead and zinc was measured. As shown in Figs. 4 and 5, both the relationship between wave height and amount of lead and zinc showed linearity.

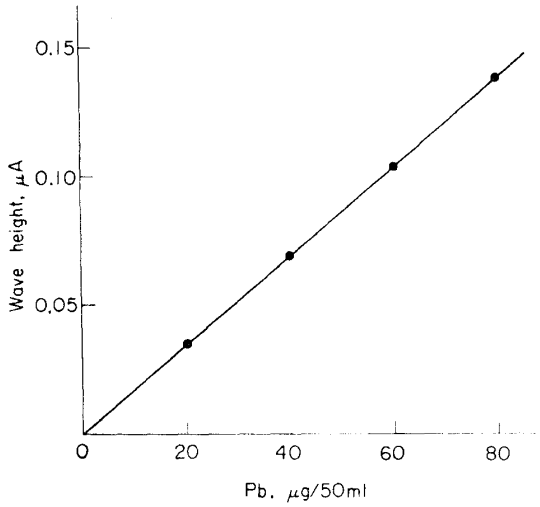

Fig. 4. Relation between wave height and amount of Pb.
Sweep rate: 0.3 V/sec, Sweep range: −0.4∼−0.85 V, Max. potential: −0.67V, Supporting electrolyte: 0.5M H_3PO_4

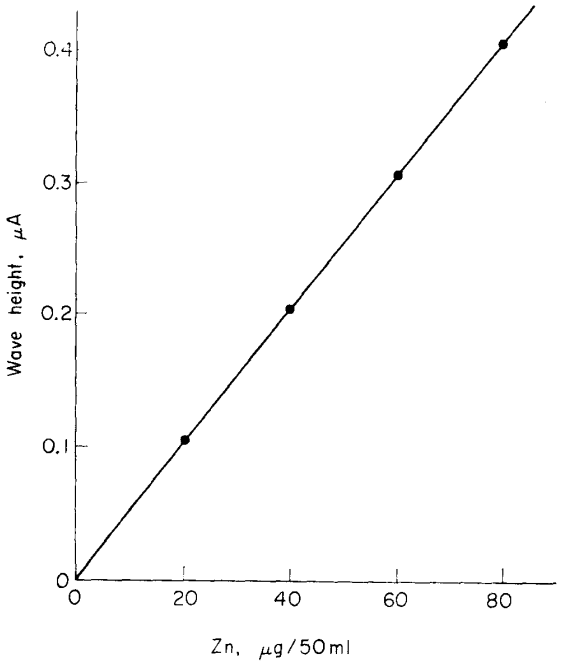

Fig. 5. Relation between wave height and amount of Zn.
Sweep rate: 0.3 V/sec, Sweep range: −1.0∼−1.45 V, Max. potential: −1.34V, Supporting electrolyte: 0.5 M H_3PO_4

4. Effect of other elements

(i) Effect of iron

Examinations were made to see what effect the main componental iron had on this method. Forty micrograms each of lead and zinc were placed in a 50-ml measuring flask, 0.5 M phosphoric acid was added, and the amount of 0～10 mg of iron was added to examine its effect. As shown in Table 1, the determination is possible in the presence of up to 5 mg of iron but, above this amount, the residual current based on a large amount of iron becomes high and the measurement will have to be made at a lower sensitivity, making it difficult to determine a minute quantity of lead and zinc.

Table 1. Effect of iron

Fe added (mg)	Wave height (μA)	
	Pb (40 μg/50 m*l*)	Zn (40μg/50 m*l*)
0	0.090	0.286
1.0	0.094	0.290
5.0	0.095	0.290
10.0	Quantitative analysis was impossible by the high residual current.	

In general, the presence of iron up to 100 times the amount of lead and zinc is permissible but in the case of iron and steel, in which the quantity of lead and zinc is extremely small, it would be necessary to separate majority of iron.

(ii) Effect of coexisting elements

Of the elements present in iron and steel, those not extracted with methyl isobutyl ketone, i.e., manganese, aluminium, copper, bismuth, cadmium, nickel, and cobalt, were measured for their peak potential and the effect of these elements on wave height of zinc and lead was examined. Each element was placed in a 50-ml measuring flask, 0.5M phosphoric acid and 1 ml of 2% gelatin solution were added, and the whole was made into a definite volume. The mixture was submitted to sweeping between –0.1 and 1.5 V to examine the peak potential of each element. Next, 30 μg each of lead and zinc were used with varied amounts of each element to obtain polarograms of lead and zinc to examine the effect of each element on their wave height. Table 2 shows the peak potential of the coexisting elements and their effect on wave height of lead and zinc.

5. Effect of methyl isobutyl ketone at the time of iron removal and its treatment

A mixture of 0.5 g of electrolytic iron and 40 μg each of lead and zinc was dissolved in a mixture of 20 ml of hydrochloric acid and 10 ml of nitric acid, the solution was evaporated to dryness to bring the acid concentration suitable for extraction, and the residue was dissolved in 25 ml of 5N hydrochloric acid. This solution was transferred to a separatory funnel using 5N hydrochloric acid and

Table 2. Effect of diverse ions

Element	Peak potential of metal ion in 0.5*M* H_3PO_4 solution (V)	Influences on Zn and Pb† waves
Al	no reduction wave	Height of Zn wave decreases with existence of more than 50 μg of Al
Mn	no reduction wave	No influence (<5000 μg)
Cu	−0.23 (II-I) −0.90 (I-0)	Height of Pb wave increases with existence of more than 100 μg of Cu. The wave of Pb becomes obscure with existence of more than 1000 μg of Cu.
Bi	−0.34	Precipitation of bismuth phosphate occurs. Height of Pb wave decreases with existence of more than 300 μg of Bi.
Cd	−0.86	No influence (<3000 μg)
Ni	−1.41	The wave of Zn becomes obscure with existence of more than 80 μg of Ni.
Co	−0.28	No influence (< 5000 μg)

† Pb and Zn taken: 30 μg/50 m*l* each

extracted with 40 ml of methyl isobutyl ketone. The organic layer was washed with 30 ml of 6N hydrochloric acid and extracted again with methyl isobutyl ketone. The combined aqueous layer was evaporated to dryness, the residue was dissolved in 0.5 M phosphoric acid, and lead and zinc were determined with this solution. In this case, the wave of zinc was not clear on account of the limiting current, which was considered to be the effect of methyl isobutyl ketone. In order to confirm this point, 40 μg each of lead and zinc with phosphoric acid as the supporting electrolyte, and 0, 1, 2, or 3 drops of methyl isobutyl ketone added were submitted to polarographic measurement.

Table 3. Influence of MIBK

MIBK added (drop)	Wave height (μA)	
	Pb (40 μg/50 m*l*)	Zn (40 μg/50 m*l*)
0	0.100	0.275
1	0.100 0.100	0.200 0.220
2	0.105 0.105	0.575 0.575
3	0.110 0.100	0.570 0.420

As shown in Table 3, the presence of methyl isobutyl ketone interfered with the wave height of zinc, though there was no effect on lead.

6. Treatment of methyl isobutyl ketone

In order to remove the interference of methyl isobutyl ketone, based on the foregoing results, the decomposition of ketone with perchloric or nitric acid was examined. To 40 μg each of lead and zinc, 5 drops of methyl isobutyl ketone were added, followed by 5 drops of perchloric acid and ca. 3 ml of nitric acid, and the mixture was heated until white fumes of perchloric acid evolved and then evaporated to dryness. This procedure of adding 5 drops of perchloric acid and ca. 3 ml of nitric acid and the subsequent evaporation to dryness was repeated a few times.

As shown in Table 4, the interference of methyl isobutyl ketone was removed by repeating the evaporation three times.

Table 4. Decomposition of MIBK (Evaporation to dryness in $HClO_4$ and HNO_3)

Number of times of drying procedures	Wave height (μA)	
	Pb(40 μg/50 m*l*)	Zn(40 μg/50 m*l*)
2	0.090 0.090 0.090	0.370 0.330 0.340
3	0.090 0.095 0.093	0.305 0.300 0.293

7. Simultaneous determination of lead and zinc in iron and steel

Based on the above-mentioned examinations, the procedure for the determination of lead and zinc in iron and steel was arranged as follows:

To 0.5~1.0 g of the sample weighed into a beaker, 20 ml of hydrochloric acid is added and the mixture is heated to effect decomposition. To this solution, 5 ml of nitric acid is added to oxidize iron and the mixture is further heated and evaporated to dryness. This residue is dissolved in 5N hydrochloric acid (which is acid concentration suitable for good extraction of iron but little of zinc) and the cooled solution is transferred to a separatory funnel using 5N hydrochloric acid. To this solution, 40~50 ml of methyl isobutyl ketone is added and the mixture is shaken thoroughly to extract iron. The separated aqueous layer is transferred to another separatory funnel (A), 30 ml of 6N hydrochloric acid (this concentration of acid is used to prevent part of iron in the ketone layer from dissolving into the acid layer) is added to methyl isobutyl ketone layer, and the mixture is shaken thoroughly to transit zinc that had been extracted into the ketone layer into the aqueous layer. The aqueous layer is transferred to a beaker (B) and the organic

layer is discarded. The aqueous layer (A) in the separatory funnel is again shaken with 40 ml of methyl isobutyl ketone to remove iron that remained unextracted, the aqueous layer is separated, and the organic layer is shaken with 30 ml of 6N hydrochloric acid. This acid layer is mixed with the previous acid solution in the beaker (B). The mixed aqueous layer is evaporated, ca. 3 ml of nitric acid and 5 drops of perchloric acid are added when the solution is evaporated almost to dryness, and further evaporated to dryness. This evaporation procedure is repeated three times.

The residue is dissolved in 5 ml of 5M phosphoric acid, 1 drop of 3% hydrogen peroxide solution being added when oxide of manganese does not dissolve, and boiled to dissolve the whole. When cooled, potassium permanganate is added until the solution becomes pink to decompose hydrogen peroxide. This solution is transferred to a 50-ml measuring flask, and 1 ml of the gelatin solution is added. Then the whole of this solution is brought to the mark with redistilled water. A part of this solution is placed in an electrolytic cell, nitrogen gas is passed through this solution for ca. 10 min to remove oxygen, and the wave height of lead and zinc is measured under the conditions of initial voltage of –0.4 V *vs.* Hg, sweeping rate of 0.3V/sec, start of sweeping of 2.0 sec, and stop of sweeping of 3.5 sec for lead, and initial voltage of –1.0V *vs.* Hg for zinc, other conditions being the same as those for lead. Quantity of lead and zinc was calculated from the calibration curve.

8. Preparation of calibration curves of lead and zinc

The caliblation curves were prepared by carrying out the analytical procedures the same as the above, using samples of the same composition as the sample for determination or the same samples with $20 \sim 80\ \mu g$ each of lead and zinc added.

9. Determination of samples

The determination was carried out by the above-mentioned analytical procedure with electrolytic iron and carbon steel with known amounts of lead and zinc added. These results and that of the determination of lead and zinc in an experimental sample are shown in Table 5.

As shown in this table, the determined amounts with synthetic samples agreed well with those of lead and zinc added. As for the precision of this method, the results obtained with nine determinations on electrolytic iron showed that the standard deviation was $\pm 0.00017\%$ and the coefficient of variation was 11.3% for lead, and that the standard deviation was $\pm 0.00063\%$ and the coefficient of variation was 15.1% for zinc.

Table 5. Analytical results of synthetic and real samples

Sample	Sample taken (g)	Pb Analytical results					Zn Analytical results				
		added		found		colorimetry (%)	added		found		colorimetry (%)
		(μg)	(%)	(μg)	(%)		(μg)	(%)	(μg)	(%)	
Electrolytic iron	0.5000	30.0	0.0060	30.2	0.0060		15	0.0030	14.8	0.0030	
		30.0	0.0060	29.7	0.0059		15	0.0030	14.8	0.0030	
		30.0	0.0060	30.2	0.0060		15	0.0030	13.5	0.0027	
〃	0.5000	10.0	0.0020	11.0	0.0022		5	0.0010	6.0	0.0012	
		10.0	0.0020	11.0	0.0022		5	0.0010	4.8	0.0010	
		10.0	0.0020	10.5	0.0021		5	0.0010	5.0	0.0010	
C-Steel	0.5000	50.0	0.010	48.3	0.0096		30	0.0060	31.0	0.0062	
		50.0	0 010	51.2	0.0100		30	0.0060	33.3	0.0067	
		50.0	0.010	49.3	0.0099		30	0.0060	33.3	0.0067	
〃	0.5000	15.0	0.0030	16.8	0.0034		10	0.0020	12.0	0.0024	
		15.0	0.0030	15.0	0.0030		10	0.0020	10.5	0.0021	
		15.0	0.0032	16.0	0.0032		10	0.0020	11.0	0.0022	
Low-C steel	0.5000			7.3	0.0015						
				7.3	0.0015						
				8.7	0.0017						
Electrolytic iron	0.5000			6.2	0.0012				20.5	0.0041	
				6.2	0.0012				20.5	0.0041	0.0038
				8.7	0.0017				23.0	0.0046	
Lead-free cutting steel	0.2000			61.8	0.031						
				59.0	0.030	0.030					
				60.0	0.030						

Summary

Cathode ray polarography was examined for the simultaneous determination of microamounts of lead and zinc in iron and steel. For the supporting electrolyte, 0.5M phosphoric acid is used and the main componental iron is removed by extraction with methyl isobutyl ketone. The contaminating methyl isobutyl ketone is removed by decomposition with perchloric and nitric acids. Peak potentials and measuring conditions were examined, and also the effect of coexisting elements. Conditions were established for simultaneous determination of microamounts of lead and zinc, and this method was applied to synthetic and experimental samples, giving a satisfactory result. Precision of this method was found to give the standard deviation of ±0.00017% and the coefficient of variation of 11.3% for lead and the standard deviation of ±0.00063% and the coefficient of variation of 15.1% for zinc.